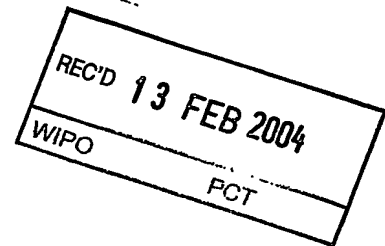


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**Prioritätsbescheinigung über die Einreichung
einer Patentanmeldung**

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Anmeldetag:	13. September 2002
Anmelder/Inhaber:	Max-Planck-Gesellschaft zur Förderung der Wissenschaften eV, München/DE
Bezeichnung:	Novel electrode materials and electrodes for Li-based electrochemical energy storage devices
IPC:	H 01 M 4/62

Die angehefteten Stücke sind eine richtige und genaue Wiedergabe der ursprünglichen Unterlagen dieser Patentanmeldung.

München, den 16. Oktober 2003
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Novel electrode materials and electrodes for Li-based electrochemical energy storage devices.

The present invention relates to the use of novel electrode materials for Li-based electrochemical energy storage devices and to novel electrodes.

In the state of the art, lithium-ion batteries and RuO_2 proton-type supercapacitors are used for rechargeable electrochemical storage devices. Among current commercial Li-ion batteries, carbon is used as an anode material, with the Li-storage capacity being less than 372 mAh/g. LiCoO_2 is used as the cathode material and has a capacity less than 150 mAh/g. For RuO_2 proton-type supercapacitors, the highest capacitance is reported as 1200 F/g, less than 200 mAh/g.

Due to the rapid development of the electronic industries, there is a great demand to increase further the energy density of electrochemical energy storage devices, leading to great interest in novel electrode materials.

Accordingly, the object of the present invention is to provide novel materials which permit a significant improvement in the electrochemical performance of Li-based electrochemical energy storage devices and electrodes for such Li-based electrochemical energy storage devices.

In order to satisfy this object, there are provided, in accordance with the invention, the uses of the materials set forth in the claims 1 to 7 and the electrodes of claims 8 to 14.

The applicants have namely found that the transition metal halides, in particular the fluorides, and also ruthenium and molybdenum oxides as well as LiF and LiO₂ when dispersed with metallic clusters can be used for Li-based electrochemical energy storage devices over a wide voltage range, for example from 0 to 4.3 V, and that they show large Li-storage capacities and good cyclic performance.

Furthermore, it has also been found that amorphous composites consisting of metal clusters and Li₂O or LiF at an atomic scale or a nanometer scale also show high reversible Li-storage behaviour.

More specifically, the following advantages can be achieved:

When the transition metal fluorides (the metal comprising one or more of the transition metals Ti, V, Cr, Ni, Mn, Fe, Co, Cu) is used as an active electrode material in an Li-based electrochemical energy storage device, high reversible capacities >500 mAh/g and sufficient cyclic performance over a wide voltage range, typically from 0-4.3V are achieved.

Furthermore it has been found that ruthenium and molybdenum oxides can be used as electrode materials for Li-based electrochemical energy storage devices and that these exhibit very high capacities, for example 1200 mAh/g, high Coulombic efficiency (typically about 100%), good reversibility over a wide voltage range (typically 0-4.3V) and high electronic conductivity.

Furthermore, amorphous composites of metal clusters and Li₂O or LiF at an atomic scale or a nanometer scale also show a high reversible Li-storage behaviour due to the extremely short diffusion lengths which are present.

The invention will now be described in more detail with reference to specific embodiments and measurements with reference to the accompanying drawings.

In the drawings there are shown:

Fig. 1 a schematic illustration of a conventional Li-ion battery,

Figs. 2A-F discharge and charge curves of fluorides/Li-cells (with $i_0 = 0.2$ mA/cm² if not mentioned),

Fig. 3 Ex situ micro-Raman spectra of TiF₃B electrodes. $\lambda = 632.8$ nm, 20x lens,

Figs. 4A-B Ex situ micro-Raman spectra (Fig. 4A) and XRD patterns (Fig. 4B) of VF₃ electrodes at different Li-insertion states,

Figs. 5A-E HRTEM images of TiF₃ electrode at different states, namely

Fig. 5A original;

Fig. 5B discharged to 0.4 V

Fig. 5C discharged to 0.0 V

Fig. 5D charged to 3.0 V

Fig. 5E charged to 4.3 V

Fig. 6 An ESR plot showing ESR spectra of TiF₃A electrode at different Li-inserted states which suggests that with insertion of Li ion, the chemical state of Li in a product of the reaction (II) is approaching to metal Li, and

Fig. 7 the ESR plots of Fig.6 in overlapped form to show intensity variation, with $T = 100\text{K}$, $Q = 3100$, Attenuation: 25, $P: 0.638\text{ mW}$.

Referring first of all to Fig. 1 it can be seen that an Li-ion battery of the commercially available kind typically comprises an anode (in this case a carbon anode) 10, a cathode 12, in this case LiCoO_2 and an electrolyte 14 disposed in the space between the anode 10 and the cathode 12. Present throughout the volume of the electrolyte are also lithium ions 16 shown as circles with a cross in the middle, and anions 18 shown as larger circles with a single line through the middle. When an external circuit is connected to the battery, current flows in the direction shown by the arrow 20.

It has already been established by others that transition metal oxides, more specifically the oxides Fe, Ni, Co, Cu, show promising performance as anode materials for rechargeable lithium batteries. The reversible Li-storage mechanism is due to the formation and decomposition of Li_2O upon the electrochemical insertion/extraction of Li (see references 1 and 2). The key point for the reversibility seems to be the formation of a special microstructure in which metal clusters are dispersed uniformly with Li_2O at a nanoscale after electrochemical reaction of metal oxide with Li (again reference is made to the references 1 and 2).

The present applicants had the idea that LiF , which is electrochemically inactive, might be able to show electrochemical activity when it is dispersed with transition metal at atomic or nanoscale level. A series of transition metal fluorides ($M = \text{Ti, V, Mn, Fe, Co, Ni, Cu}$) have been inves-

tigated and the present description shows the results on TiF_3 and VF_3 as examples. SnF_2 and $(\text{CF}_x)_n$, $x=1$ are also presented for comparison.

The experimental setup was as follows:

The working electrodes comprised **TiF3A**: TiF_3 : PVDF (9:1) on Ti foil; **TiF3B**: TiF_3 : CB: GP: PVDF (10:1:1:1) on Ti foil. Throughout this specification and drawings CB denotes carbon black, GP denotes graphite and PVDF denotes polyvinylene di-fluoride.

The electrochemical cells tested were 2-electrode cells for electrochemical testing similar in layout to the known cell of Fig. 1 but using the alternative electrodes. It is noted that the electrode materials proposed and claimed here can be used as either anodes or cathodes depending on the relative potential difference to the metal lithium. If this potential difference is 2.5 volts or less then the material is considered suitable as an anode material. If the potential difference is 2.5 volts or more then the material is considered suitable as a cathode material. The electrolyte was:

1M LiPF_6 , EC-DMC(1:1), Merck, i.e. 1 molar lithium phosphorous fluoride 6, ethylene carbonate-dimethyl carbonate available from Merck, and the investigation was carried out using HRTEM and micro-Raman with procedures similar to those described in the papers by H. Li, X. J. Huang, L. Q. Chen, *Electrochem. Solid-State Lett.*, 1, 241(1998) and H. Li, Y. Mo, N. Pei, X. Xu, X. J. Huang, and L. Q. Chen, *J. Phys. Chem. B* 104, 8477(2000).

Moreover, a special electrochemical cell was designed for the control of the Li-insertion state and for a subsequent pseudo in-situ ESR experiment. The interference from the electrolyte and Li electrode can be avoided. The

TiF3A type electrode was used for ESR and HRTEM and the TiF3B type electrode was used for micro-Raman.

Figs. 2A to 2F show the discharge and charge curves that were achieved for Li cells utilising TiF₃ electrodes (Figs. 2A and 2B) and VF₃ electrodes (Figs. 2C and 2D) and also for SnF₂/Li electrodes (Fig. 2E) and CF_xn lithium electrodes (Fig. 2F).

The voltage profile of the discharge curves exhibits plateau region at high voltage and slope region at low voltage. The capacity of the plateau region is close to the theoretical capacity of decomposition reaction of fluorides, which is reversible in the cases of TiF₃ and VF₃. The slope regions for SnF₂, TiF₃ and VF₃ are also reversible, but the former is caused by the Li-Sn alloy reaction (see reference 5), while later (about 250 mAh/g) is related to the insertion of Li into the matrix of LiF/M. Interestingly, (CF_x)_n also shows partial reversibility. The theoretical capacity and voltage for the decomposition reactions (Plateau region) are as follows:

TiF₃: 767 mAh/g, 1.396 V; VF₃: 745 mAh/g, 1.863 V;

SnF₂: 342 mAh/g, 2.984V; (CF_x)_n, x=1: 865 mAh/g, 2.9V.

The results of Raman spectroscopy and XRD investigations are shown in Figs. 3 and 4.

In Fig. 3 phase transitions are observed from the crystal to the amorphous state with Li insertion and back to the original phase with Li extraction.

Fig. 4 shows ex situ Raman spectra (Fig. 4A) and XRD patterns (Fig. 4B) of VF₃ electrodes at different Li insertion states.

Turning now to Fig. 5 there are shown HRTEM images of TiF₃ electrodes at different states. The five states, Fig. 5A to Fig. 5F are as follows:

5A: Original; 5B: discharged to 0.4 V; 5C: discharged to 0.0 V;
5D: charged to 3.0 V; and 5E: charged to 4.3 V.

The crystal parameters are as follows:

TiF₃: Rhombohedral, d_{110} : 0.388 nm, d_{101} : 0.274 nm, d_{210} : 0.233 nm,
 d_{200} : 0.223 nm

Ti: Hexagonal, d_{010} : 0.256 nm, d_{002} : 0.234 nm, d_{011} : 0.224 nm.

Li: Cubic, d_{110} : 0.248 nm, d_{200} : 0.176 nm.

LiF: Cubic, d_{111} : 0.233 nm, d_{200} : 0.201 nm;

Finally, Figs. 6 and 7 show ESR spectra of TiF₃A electrode at different Li-inserted states (Fig. 6) and the same diagrams overlapped (Fig. 7) to show intensity variation. The following parameters apply here:

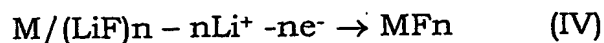
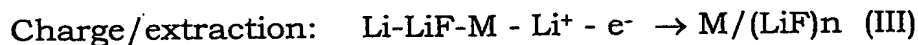
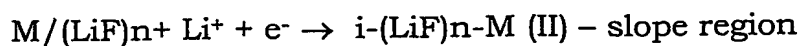
$T = 100$ K, $Q = 3100$, Attenuation: 25, $P = 0.638$ mW,

The ESR results suggest that with insertion of Li ions, the chemical state of Li in the product of the reaction (II) is approaching to metal Li.

From these results, the following conclusions can be drawn:

1. The following electrochemical reactions occur between transition metal fluorides and Li at a wide voltage range (0-4.3V), besides the formation of the solid electrolyte interphase (SEI) film and intermediate Li transition metal fluorides in the cases of Ti, V, Fe (which form Li_{0.5}MF₃):

Discharge/insertion: $MF_n + nLi^+ + ne^- \rightarrow M + nLiF$ (I) - plateau region,



2. We propose that the extra capacity at the slope region for fluorides is mainly due to the distribution of Li within the matrix of LiF/M rather than the formation of the SEI film (see reference 2). This needs further confirmation.

3. Microstructure of the products in the reaction (I) and (II) is amorphous, which may indicate an atomic-scale dispersion of metal and LiF. This is a key factor for the extraction of Li from LiF.

4. The reversibility of the reaction (IV) is related to metal type and conductive additive (kinetic problem).

Further background information can be found from the following documents:

1. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, *Nature*, 407, 496(2000)
2. S. Laruelle, S. Grugeon, P. Poizot, M. Dolle, L. Dupont, J-M. Tarascon, *J. Electrochem. Soc.*, 149, A627(2002)
3. H. Li, L. H. Shi, W. Lu, X. J. Huang, L. Q. Chen, *J. Electrochem. Soc.* 148, A915(2001).
4. H. Arai, S. Okada, Y. Sakurai, J. Yamaki, *J. Power Sources*, 68, 716(1997)
5. H. Li, L. H. Shi, W. Lu, X. J. Huang, L. Q. Chen, *J. Electrochem. Soc.* 148, A915 (2001)

6. H. Arai, S.Okada, Y. Sakurai, J. Yamaki, J. Power Sources, 69, 716 (1997)

Patent Claims

1. Use of at least one transition metal halide with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres as an electrode in an Li-based electrochemical energy storage device.
2. The use of claim 1, wherein the halide is a fluoride.
3. The use in accordance with claim 1 or claim 2, wherein said transition metal is chosen from the group comprising Ti, V, Cr, Ni, Mn, Fe, Co, Cu.
4. The use of at least one ruthenium oxide with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres as an electrode material for an Li-based electrochemical energy storage device.
5. The use of at least one molybdenum oxide with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres as an electrode material for an Li-base electrochemical energy storage device.

6. The use of a mixture of ruthenium and molybdenum oxides with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres as an electrode material for an Li-based electrochemical energy storage device.
7. The use of an amorphous composite of metal clusters and Li_2O or LiF at an atomic scale or a nanometer scale to provide a highly reversible lithium storage behaviour.
8. An electrode for an Li-based electrochemical energy storage device, the electrode comprising at least one transition metal halide with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres.
9. The electrode of claim 8, wherein the halide is a fluoride.
10. An electrode in accordance with claim 8 or claim 9, the electrode comprising a transition metal chosen from the group comprising Ti, V, Cr, Ni, Mn, Fe, Co, Cu.
11. An electrode for an Li-based electrochemical energy storage device, the electrode comprising at least one ruthenium oxide with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres.

12. An electrode for an Li-based electrochemical energy storage device, the electrode comprising at least one molybdenum oxide with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres.
13. An electrode for an Li-based electrochemical energy storage device, the electrode comprising a mixture of ruthenium and molybdenum oxides with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres.
14. An electrode for an Li-based electrochemical energy storage device, the electrode comprising an amorphous composite of metal clusters and Li_2O or LiF at an atomic scale or a nanometer scale to provide a highly reversible lithium storage behaviour.

Abstract

The description relates to the use of at least one transition metal halide with a binder, e.g. at least one of PVDF, PTFE, PAN and ETDM and optionally with at least one conductive additive such as carbon black, graphite, metal powder and metal fibres as an electrode in an Li-based electrochemical energy storage device. Further electrode materials are also described based on ruthenium oxide, molybdenum oxide, lithium fluoride and lithium oxide.

A sketch of Li ion batteries:

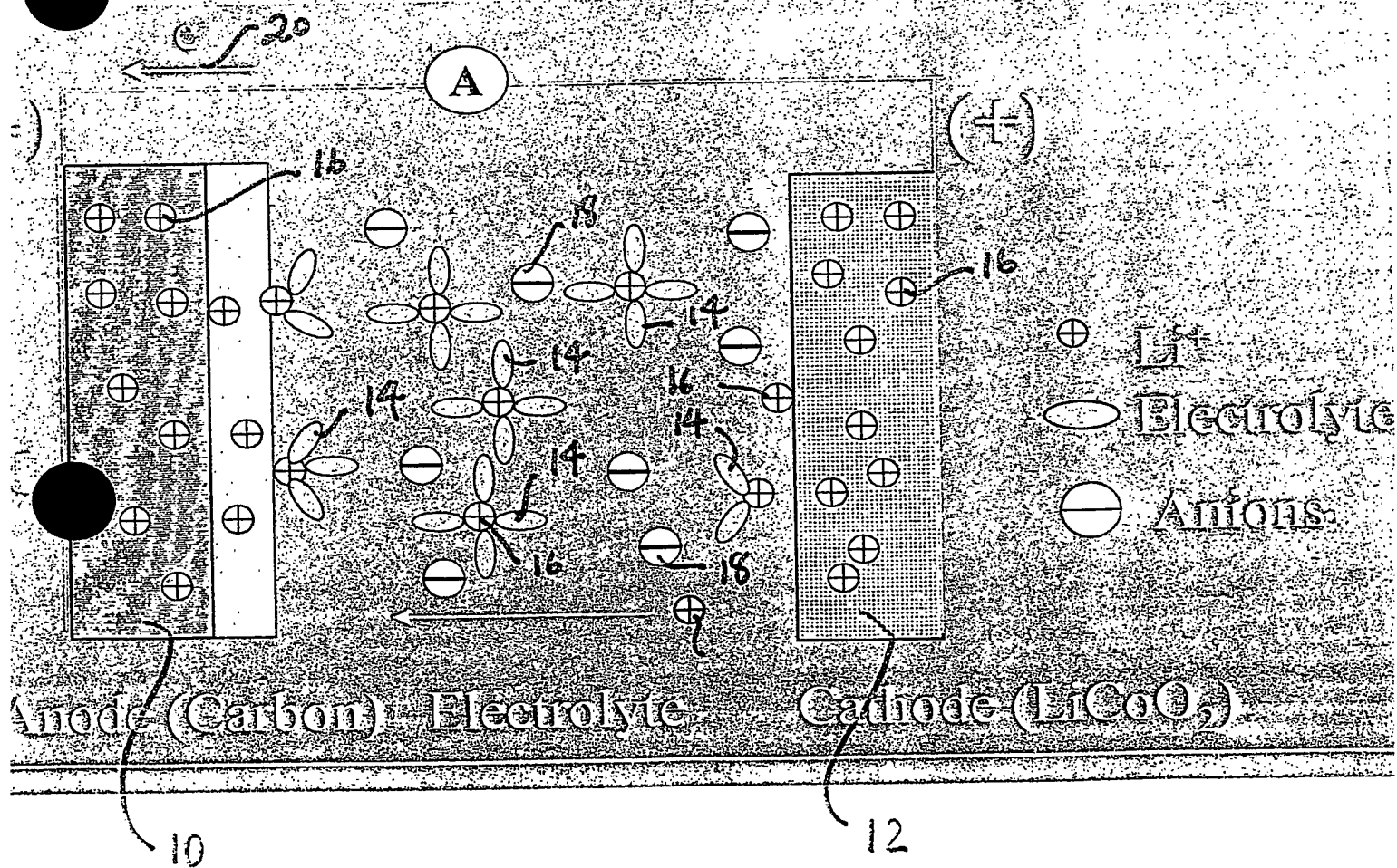


FIG. 1

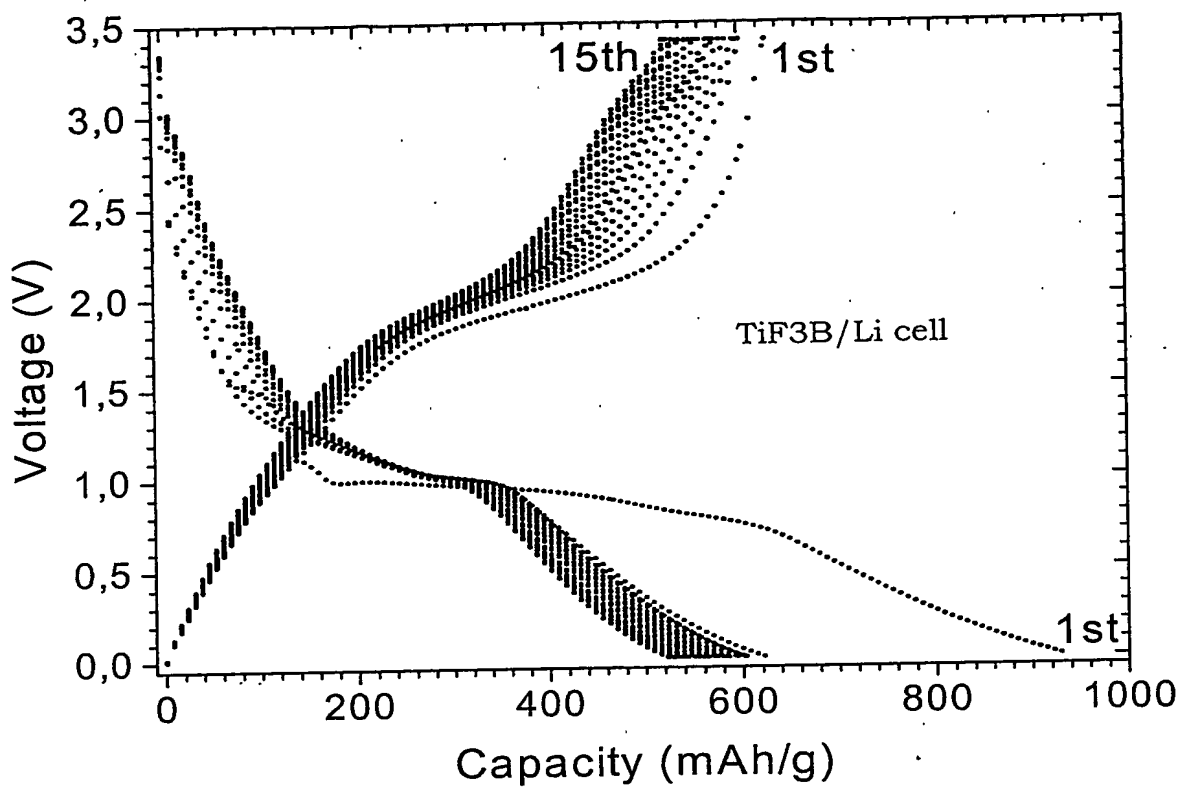


FIG. 2A

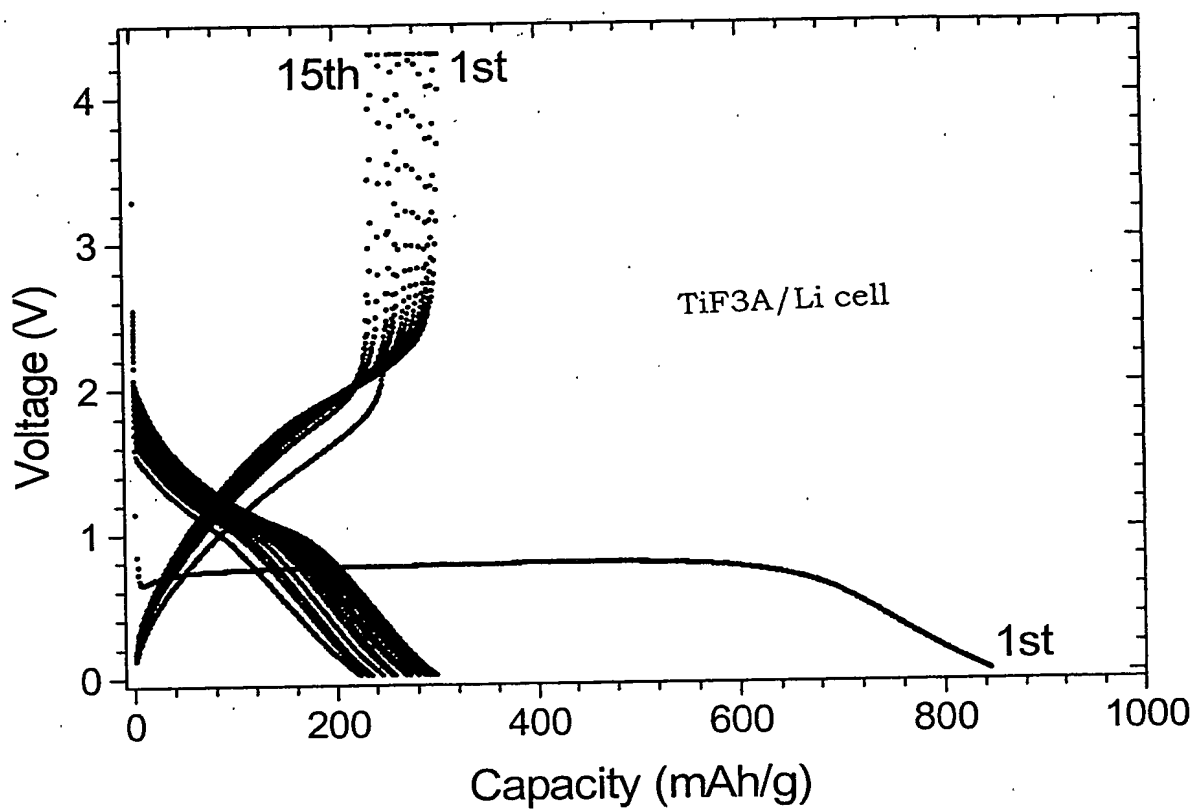


FIG 2B

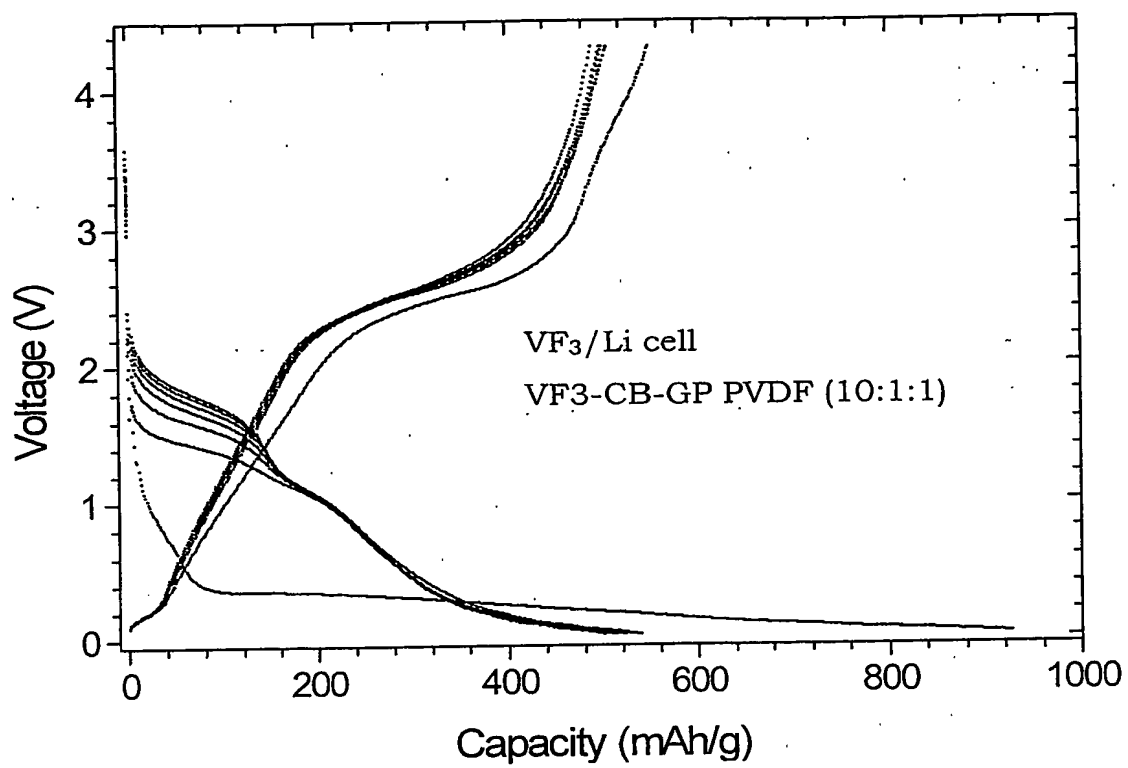


FIG 2C

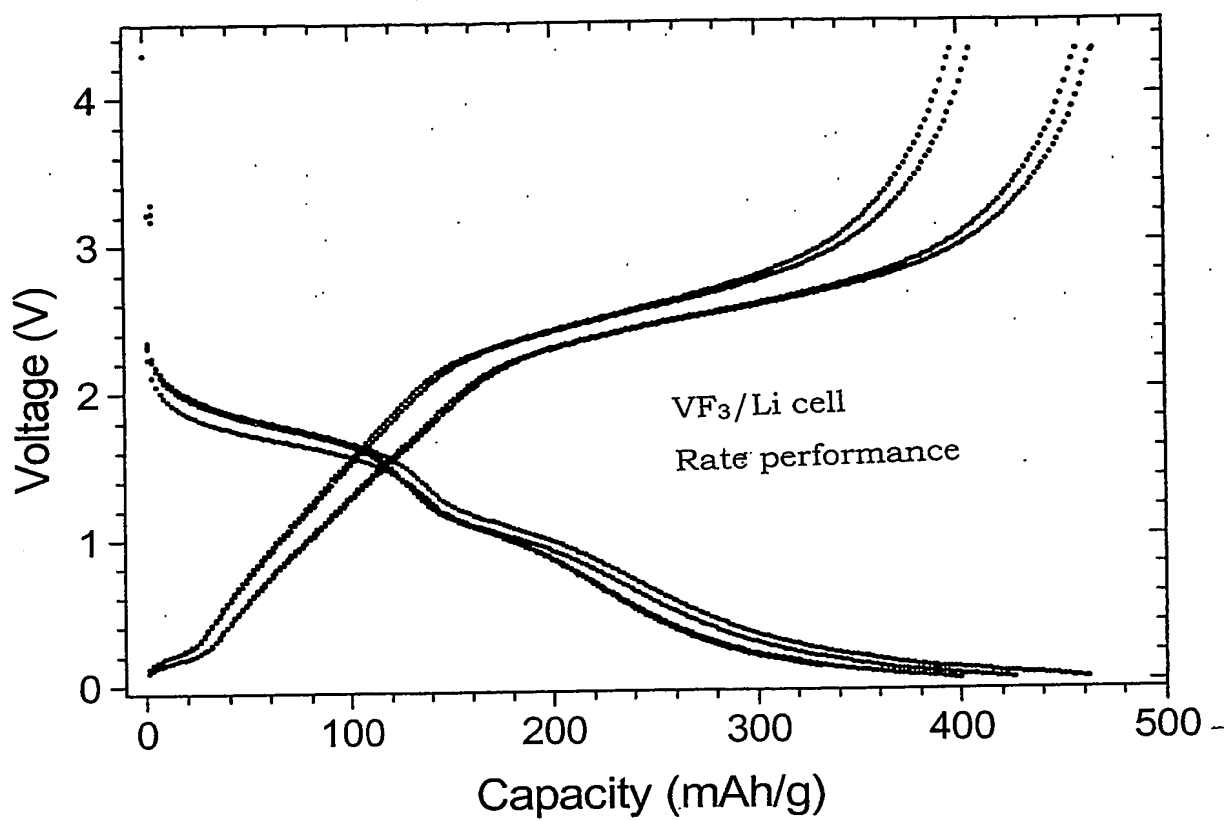


FIG 2D

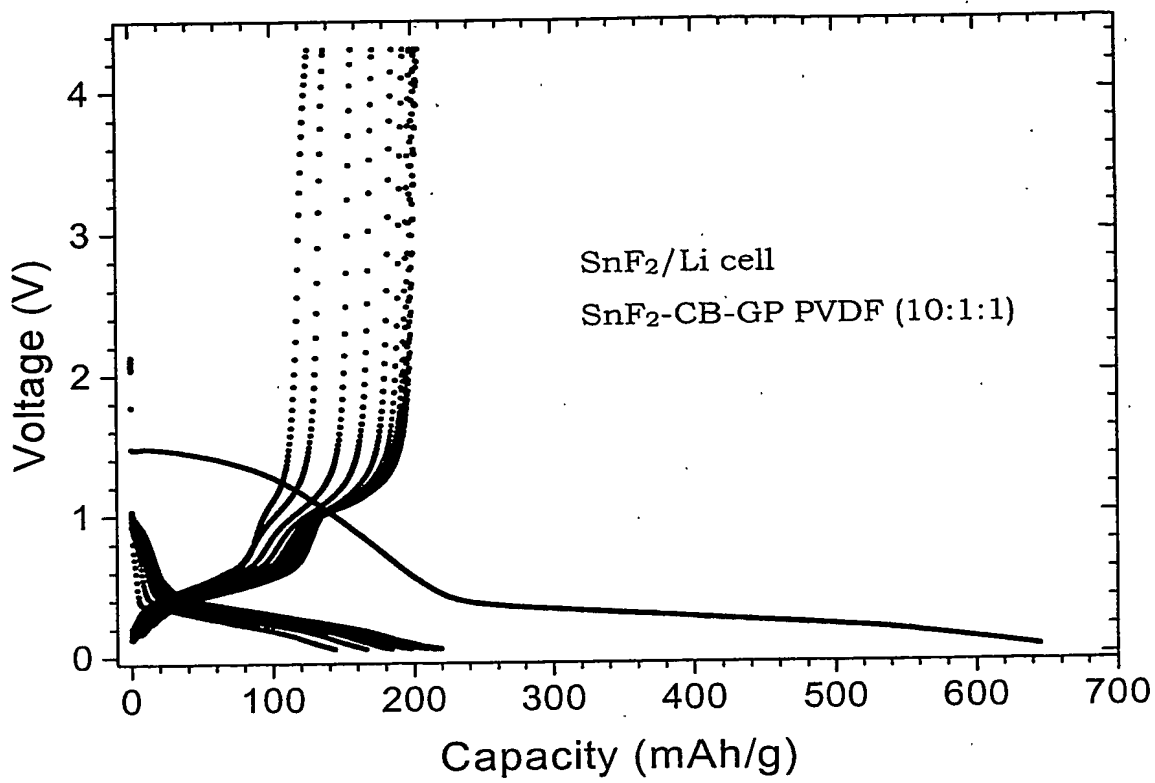


FIG 2 E

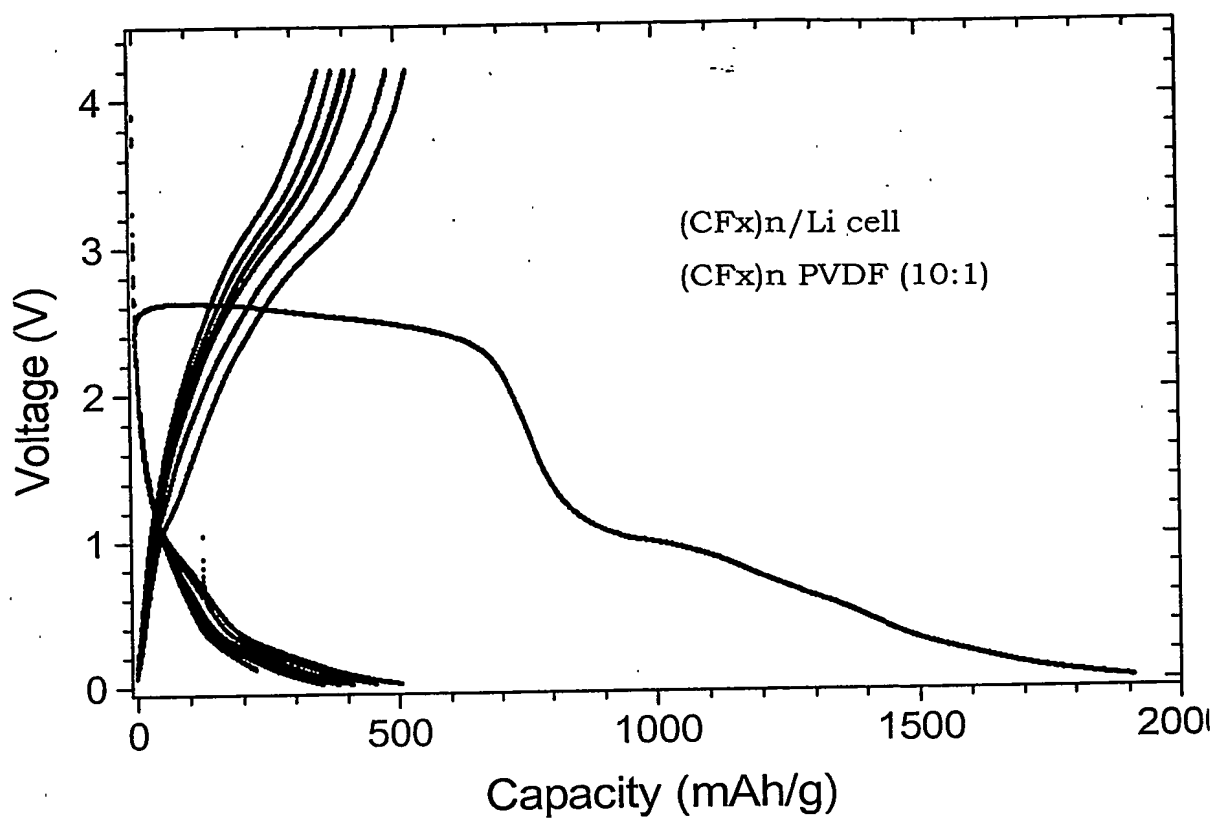


Fig. 2F

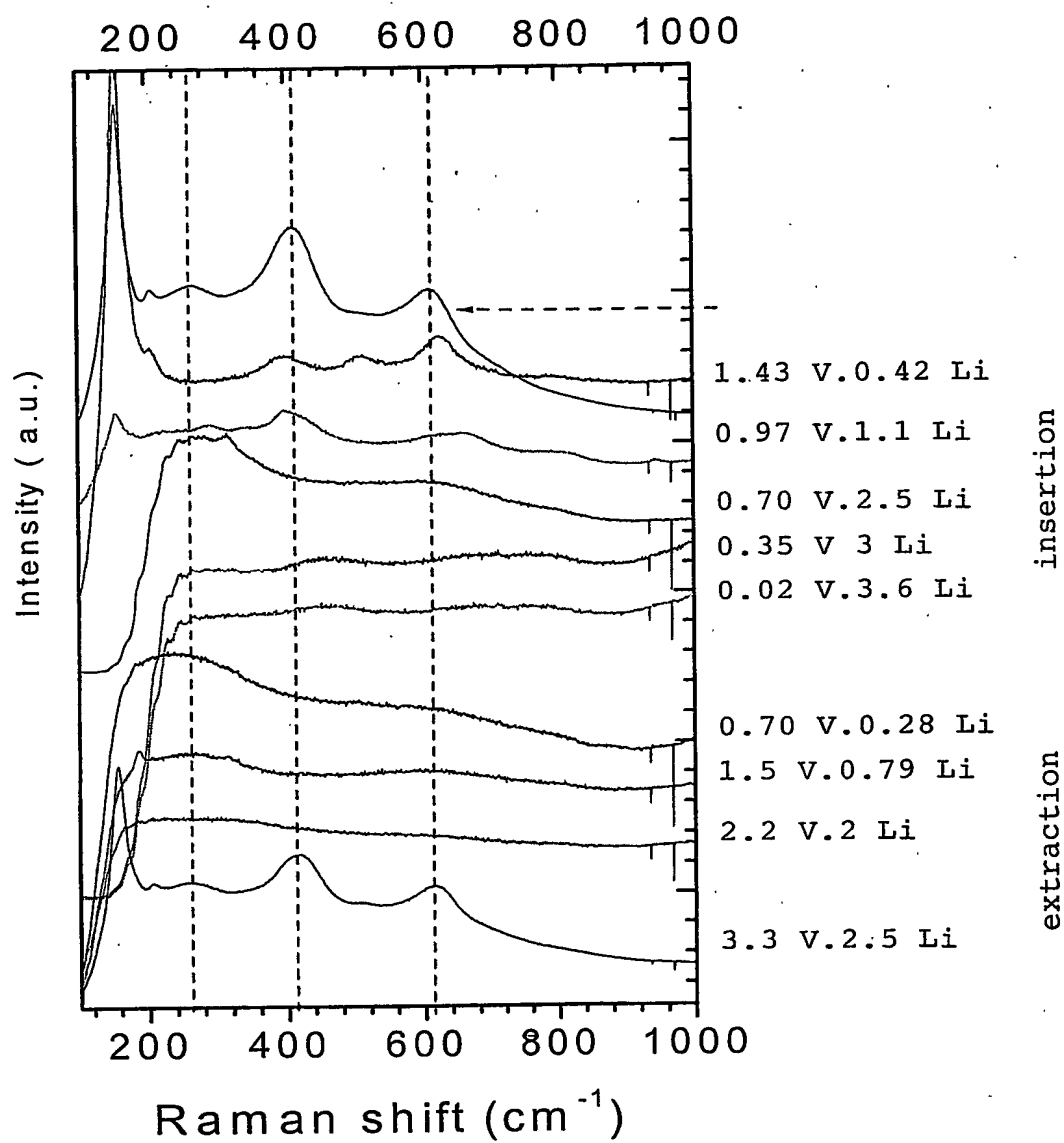


FIG 3

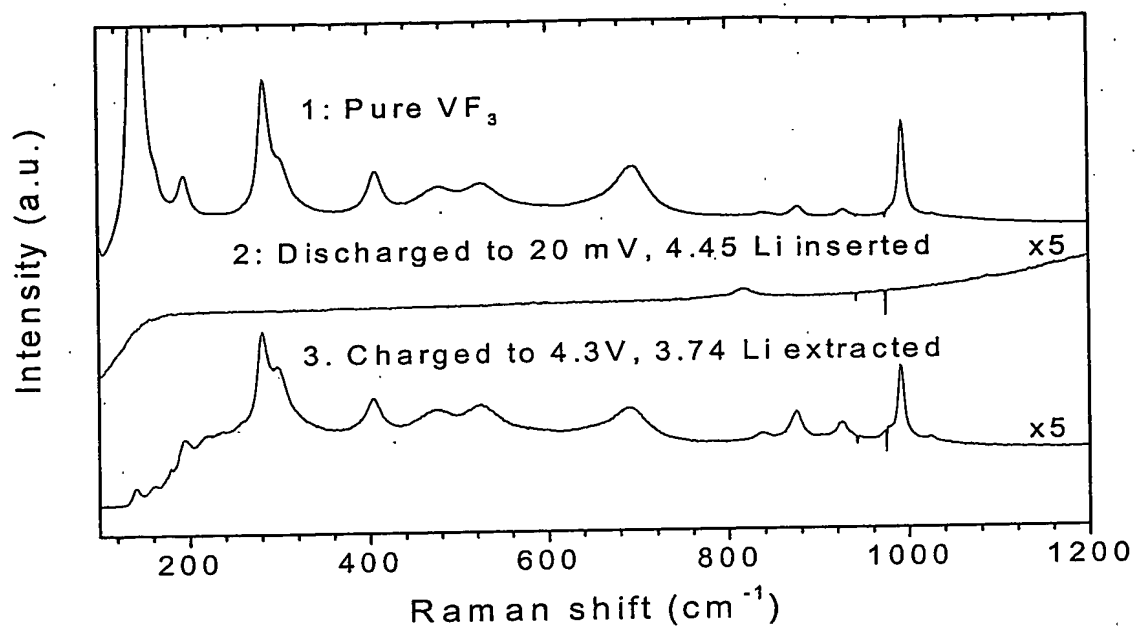


FIG. 4 A

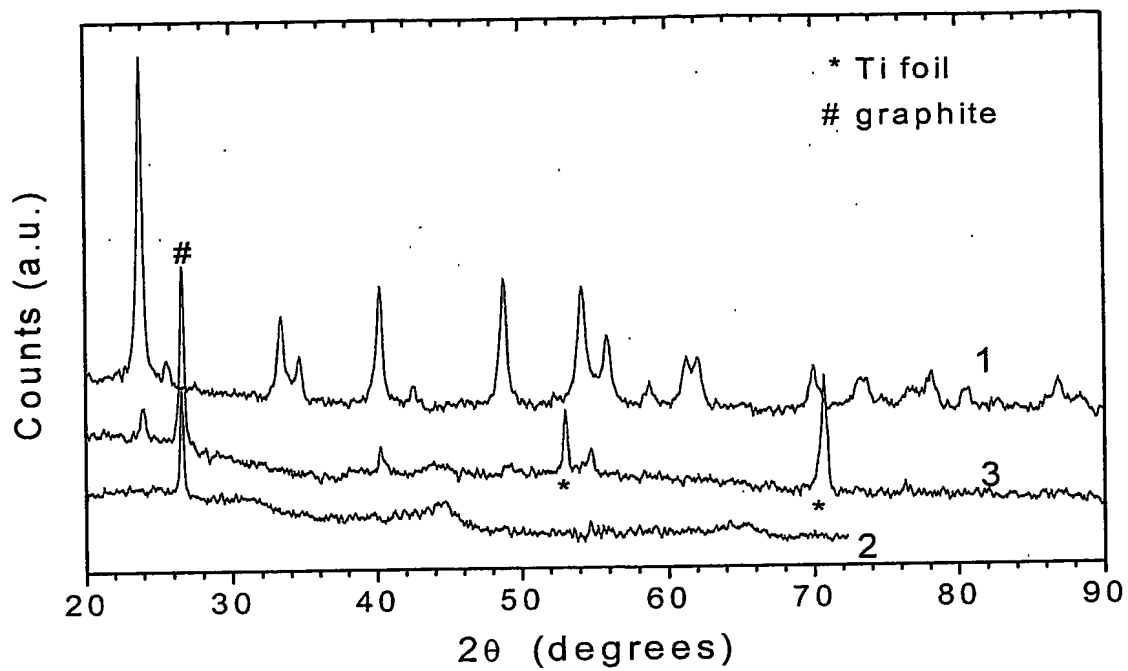


FIG 4B

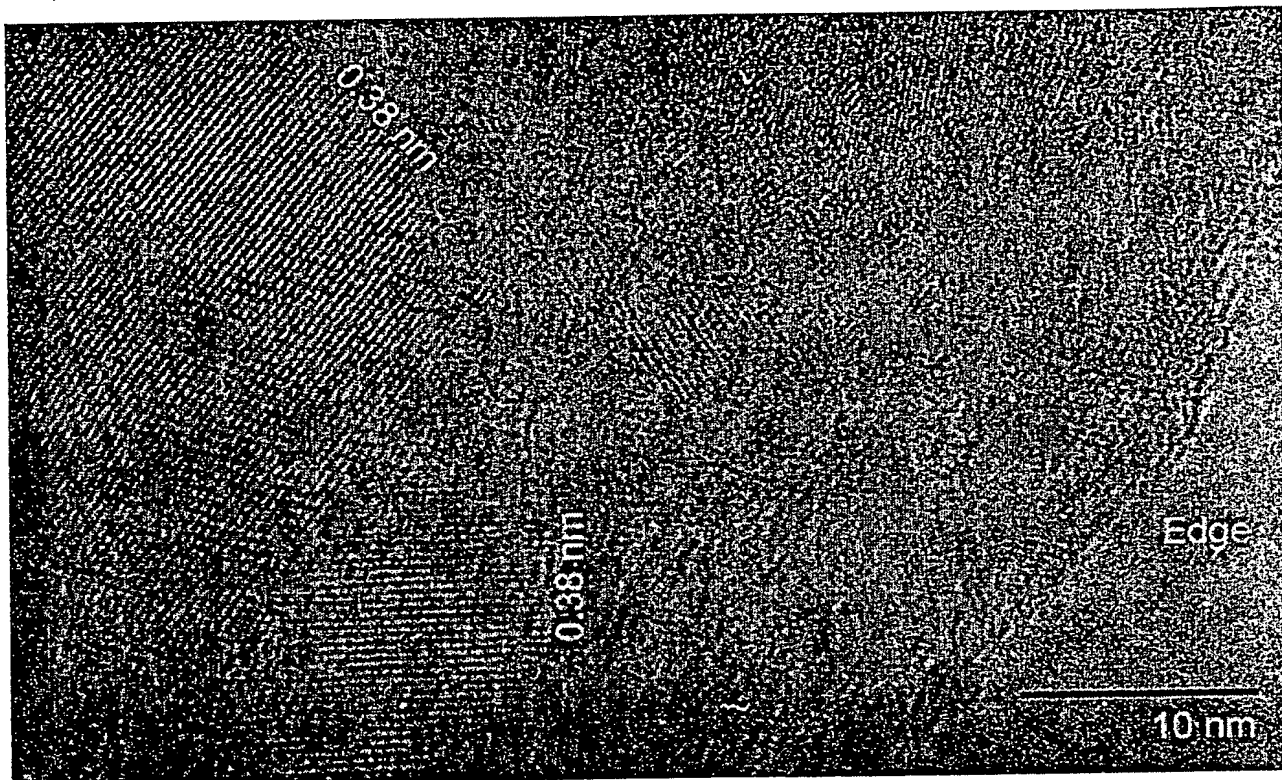


FIG 5A

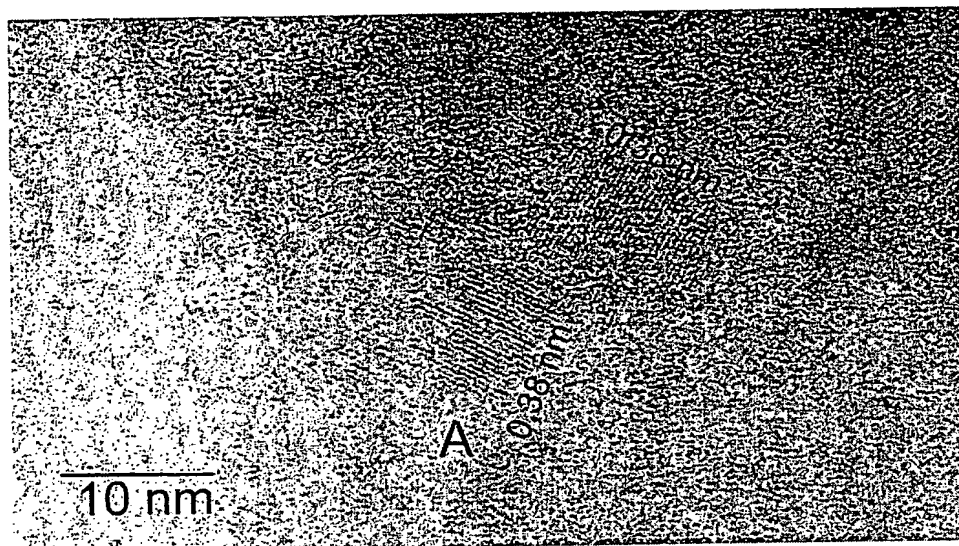


FIG 5B

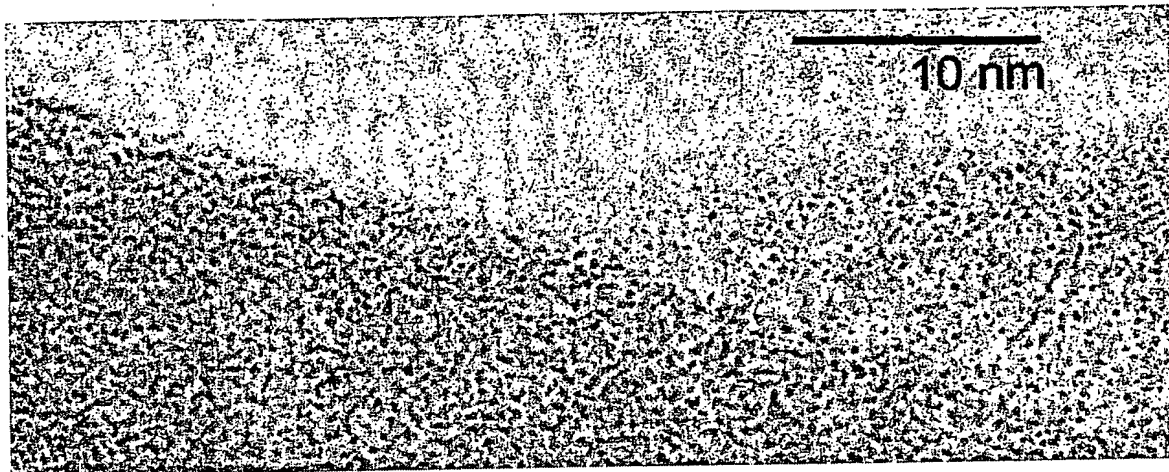


FIG 5C

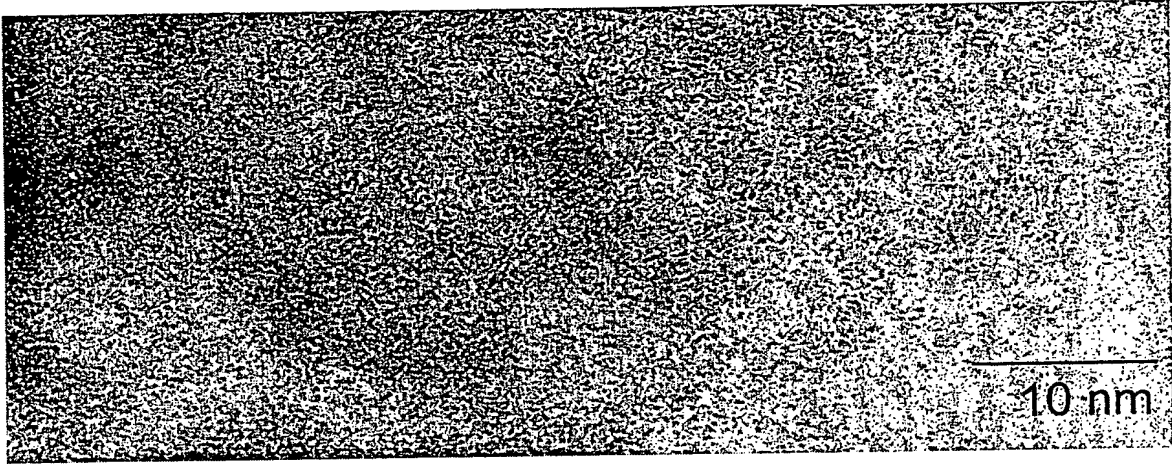


FIG 5 D

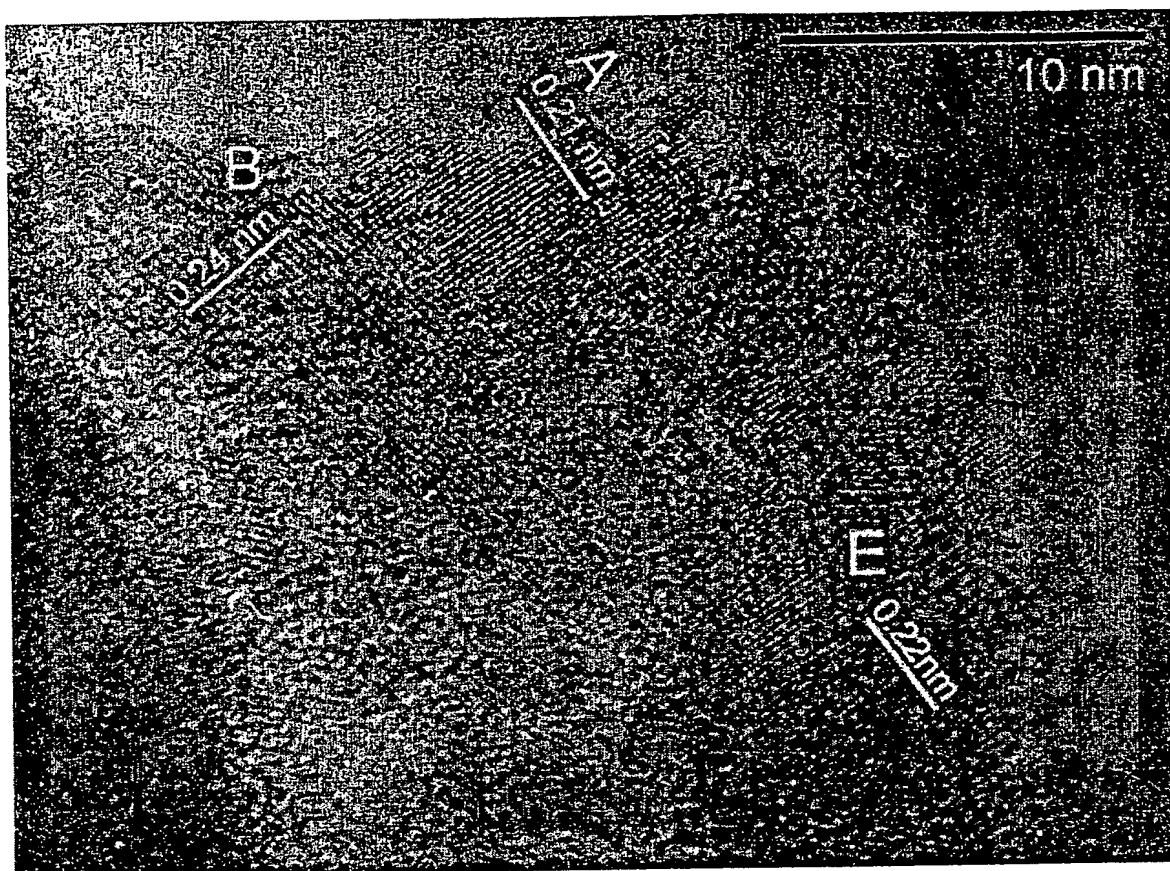


FIG 5E

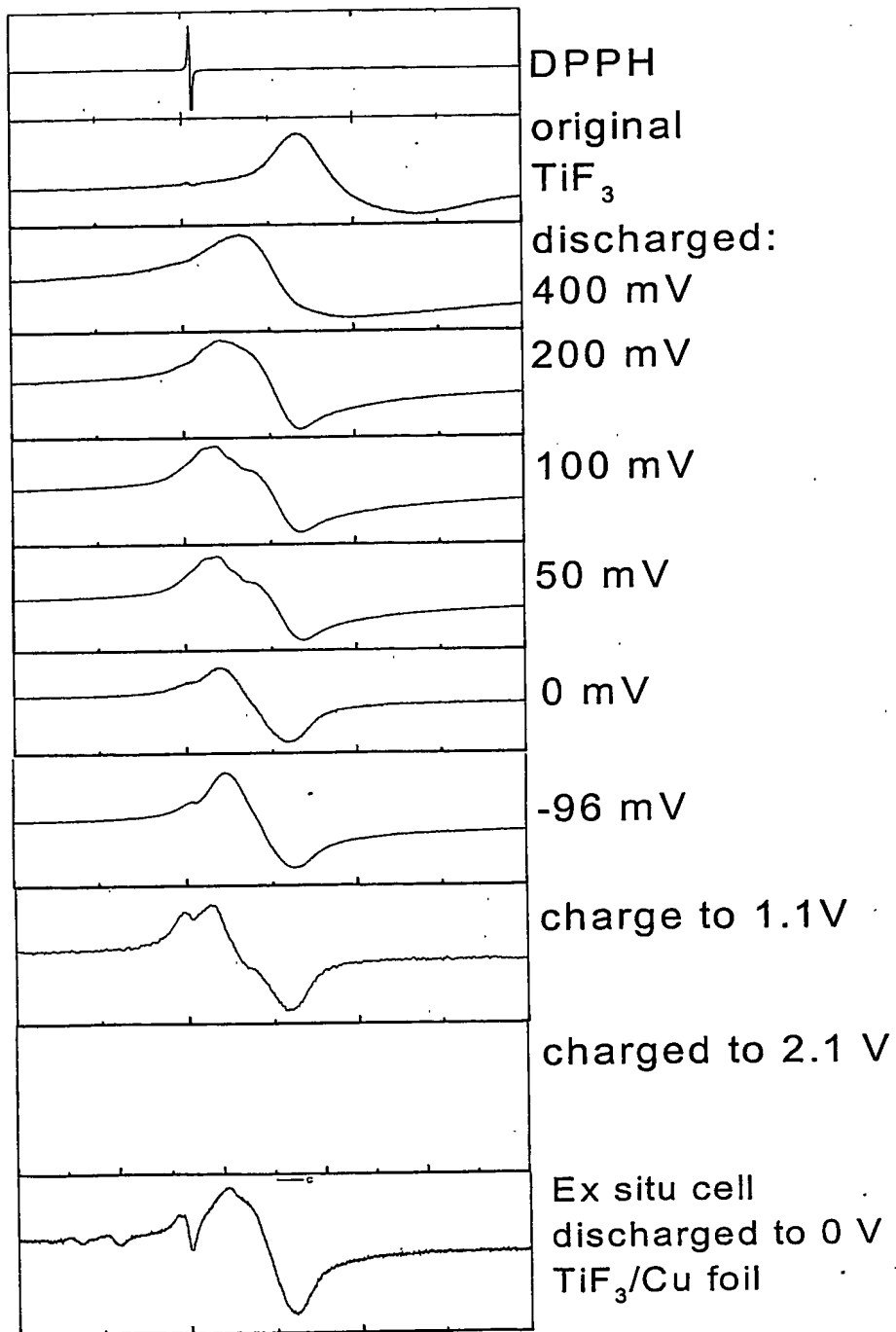


FIG 6

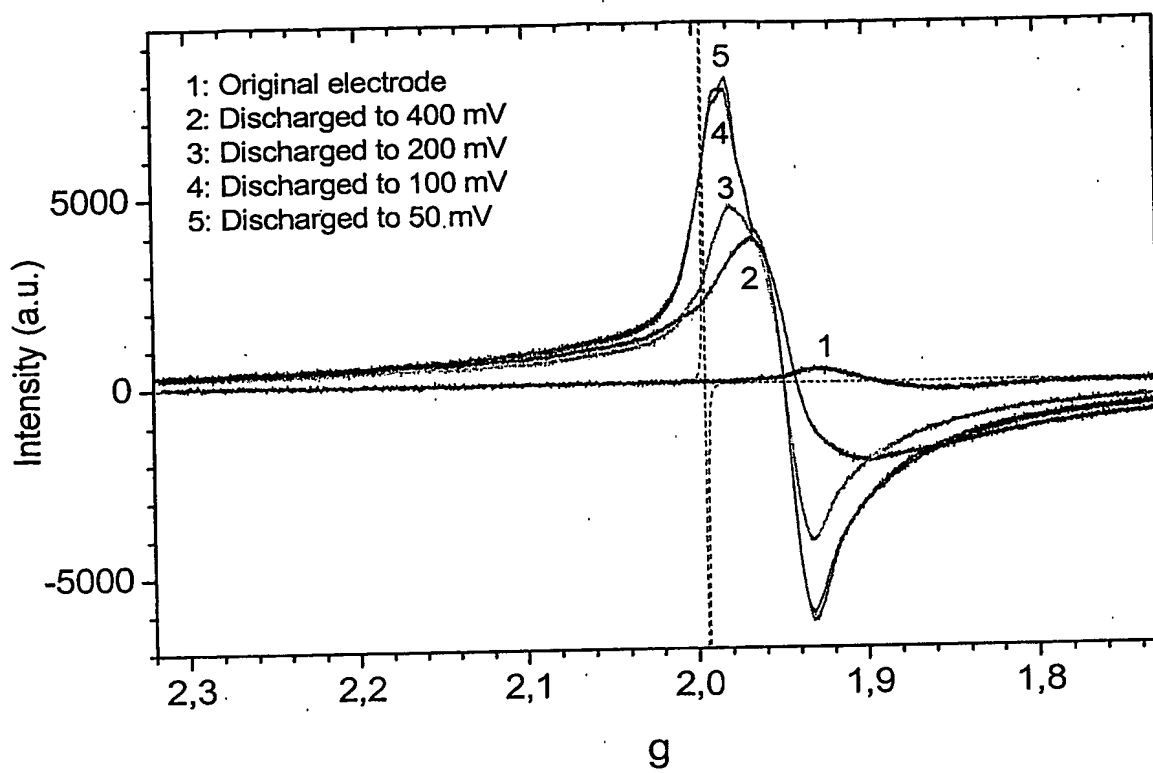


FIG 7

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